

SYNTHESIS AND CHARACTERIZATION OF RuO₂/POLY (3,4-ETHYLENEDIOXYTHIOPHENE) (PEDOT) COMPOSITE NANOTUBES FOR SUPERCAPACITORS

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Abstract: We report the synthesis of composite RuO₂/(3,4-ethylenedioxythiophene) (PEDOT) nanotubes with high specific capacitance and fast charging/discharging capability as well as their potential application to the electrode materials for a high-energized and high-powered supercapacitor. We show that the energy density (specific capacitance) of PEDOT nanotubes can be remarkably enhanced by electrodepositing RuO₂ into their porous walls and onto their rough internal surfaces. The flexible PEDOT prevents the RuO₂ from breaking while the rigid RuO₂ keeps the PEDOT nanotubes from collapsing and aggregating. The composite RuO₂/PEDOT nanotube can reach a high power density of 20 kW/kg while maintaining 80% of its energy density (28 Wh/kg). This high power capability is attributed to the fast charge/discharge of nanotubular structures. The high energy density is benefited from the RuO₂, of which the high specific capacitance (1217 F/g) is realized owing to its high specific surface area brought by the nanotubular structures.

Keywords: Supercapacitor, nanotube, template synthesis, PEDOT, ruthenium oxide, specific capacitance, electrochemical deposition

INTRODUCTION

Supercapacitors, also known as electrochemical capacitors, or ultracapacitors, have received growing attention because of their higher power delivery or uptake than batteries. Depending on the charge storage mechanism as well as the active materials used, supercapacitors can be distinguished as two major types: (1) an electrochemical double-layer capacitor (EDLC) that stores the energy non-faradaically by charging an electrochemical double layer at the interface between the porous electrode and the electrolyte, and (2) a redox supercapacitor or pseudo capacitor that stores energy faradaically using the pseudocapacitance behaviour of a redox-active material. More recently, more research has been concentrated on investigating the redox supercapacitors because the specific pseudo-capacitance exceeds that of carbon materials using double layer charge storage.

Transition metal oxides as well as electrically conducting polymers are typical examples of pseudo-capacitive active materials. In order to achieve high power at high charge/discharge rate, the fast conversion rate of the redox states has to be maintained. Because the conversion rate between redox states is governed by ion diffusions, failure to maintain the fast ion diffusions during the fast charging/dischARGE process at high power demand will cause incomplete utilization of the electrode material,

i.e. a loss of usable energy. Nanomaterials, which allow fast ion diffusions owing to their small sizes, have been proposed and successfully applied in redox supercapacitors to address the above problems. The small diameters of 1-D nanomaterials along their axes provide high surface area and enable the rapid redox processes of electroactive materials by providing short diffusion distances for the ions.

In our previous paper, we have successfully demonstrated high-powered poly(3,4-ethylenedioxythiophene) (PEDOT) nanotubes as electrode materials for high-powered supercapacitors. The energy density of supercapacitors composed of the PEDOT nanotubes is restricted by the moderate specific capacitance of PEDOT (140 F/g), which is an intrinsic property of the PEDOT itself. Doping PEDOT with materials that have high specific capacitance has been used to address this problem. For example, in our recent paper, we have successfully improved the specific of capacitance of PEDOT up to 210 F/g by fabricating the composite MnO₂/PEDOT coaxial nanowires.

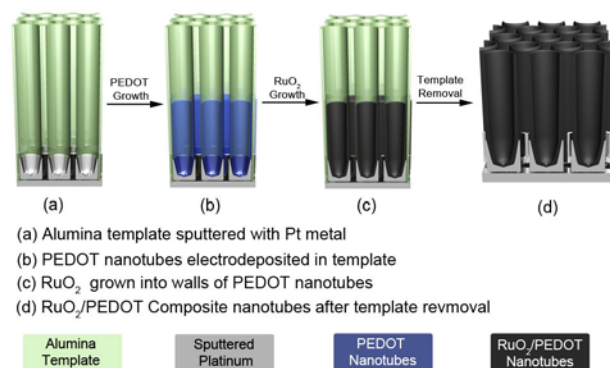
In this paper, we will report the step-wise template synthesis of RuO₂/PEDOT nanotubes, which can further enhance the specific capacitance of PEDOT nanotubes to 640 F/g brought by high specific capacitance of RuO₂ (1217 F/g), while maintaining the high power (20 kW/kg) featured by the nanotubular structures.

THEORY

An alumina template is used to direct the growth of PEDOT nanotubes by electropolymerization, and then the RuO₂ are electrodeposited into the porous network of the PEDOT nanotubes to form composite RuO₂/PEDOT nanotubes. Such further deposited RuO₂ utilizes the free void spaces available in the PEDOT nanotubes and exhibited high specific capacitance realized by the high specific surface area benefited from the nanotubular structures. Microscopic characterizations reveal that the PEDOT nanotubes indeed serve as the template to direct the growth of RuO₂ onto their rough porous internal surface. Furthermore these flexible PEDOT nanotubes can prevent the RuO₂ nanostructures from breaking after template removal. At the same time, the more rigid RuO₂ helps the PEDOT nanotubes to maintain their nanotubular shapes by keeping them from collapsing. Cyclic voltammetry was used to qualitatively analyze the capacitive properties of composite RuO₂/PEDOT nanotube based electrode. The specific capacitance, energy densities and power densities were evaluated by galvanostatic charge/discharge cycling for the supercapacitor.

RESULTS AND DISCUSSION

The synthesis of RuO₂/PEDOT can be illustrated in Scheme 1. First, the PEDOT nanotubes can be grown on the ring-shaped bottom electrodes at high over potential (>1.4 V) under low EDOT concentration (<50 mM) based on our previous proposed mechanism: the bottom ring shape electrode defines the tube shapes and the limited diffusion of monomer with low concentration preventing the formation of solid nanowires. In this paper, we have electrodeposited 300 mC/cm² of PEDOT, which corresponds to a 0.18 mg/cm² mass loading. The hollow PEDOT nanotubes allow the penetration of RuCl₃ (20 mM) solution into their voids so that the hydrous RuO₂ can be further electrodeposited onto the rough internal surfaces of PEDOT nanotubes using a cyclic voltammetry method that cycled between -0.2 V to 1V at 50 °C. The detailed growth process of RuO₂ can be found elsewhere. Figure 1 shows the cyclic voltagram of RuO₂ growth on PEDOT nanotubes by the first 40 cycles. As the cycle number increases, both anodic and cathodic current increase, which corresponds to the continuous growth of RuO₂. Therefore the loading amount of RuO₂ can be controlled by the cycle numbers.



Scheme 1. Step-wise electrodeposition of RuO₂/PEDOT composite nanotubes in alumina template

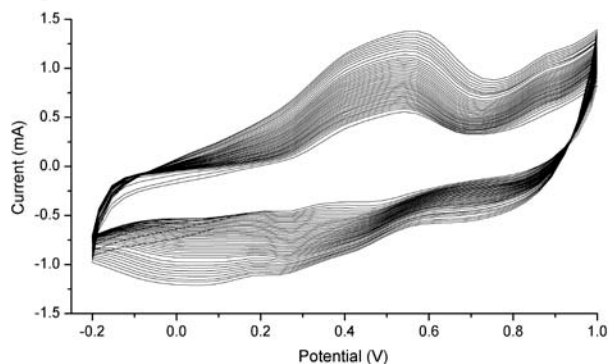


Figure 1. Cyclic voltammetry growth of RuO₂ into PEDOT nanotubes between at the scan rate of 50 mV/s in 20 mM RuCl₃ solution at 50 °C.

Figure 2a shows the SEM image of typical PEDOT nanotubes after template removal, which have a similar appearance as before: highly collapsed and aggregated structures, which are caused by the intensive aggregation of nanostructures at their tops driven by the strong surface tension generated at the interface between the nanotubes and solvent during the solvent evaporation. As we can see, top parts of the PEDOT nanotubes are collapsed into belts shape. Figure 2b shows the SEM image of RuO₂ nanorods after template removal. Due to the brittle nature of metal oxide, these RuO₂ nanorods are found to be broken either at their bottoms or in the middle. Figure 2c shows the SEM of RuO₂/PEDOT composite nanotubes. Some open entrances can be clearly found at the top of these composite nanotubes. Compared to the closed tips of PEDOT nanotubes shown in Figure 2a, we can see that the inclusion of rigid RuO₂ help the soft PEDOT nanotubes from collapsing into belts shapes effectively. On the other hands, much less breakage is found for the composite nanotubes compared to the Figure 2b, which is offered by the added flexibility of PEDOT to the rigid RuO₂.

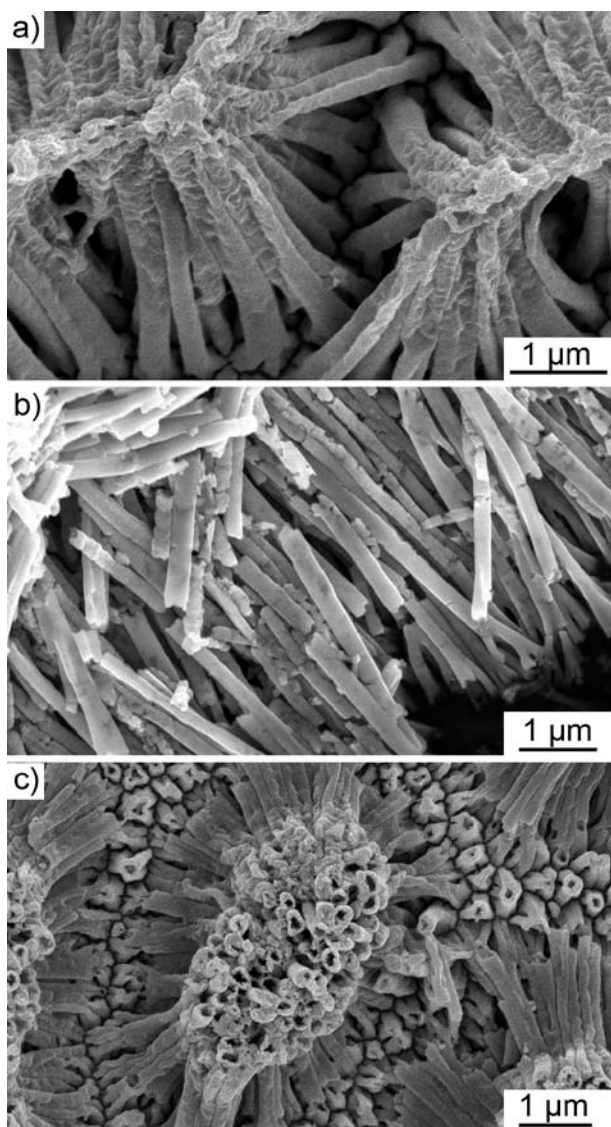


Figure 2. SEM images of a) PEDOT nanotubes electrodeposited by the charge density of 300 mC/cm² after template removal b) RuO₂ nanowires electrodeposited by 120 CV cycles c) RuO₂/PEDOT nanotubes after template removal.

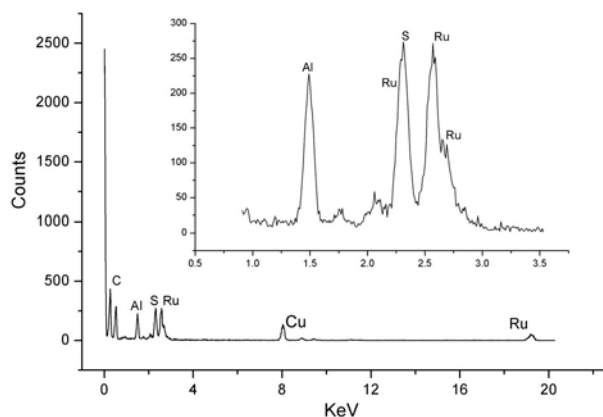


Figure 3. EDS analysis of RuO₂/PEDOT composite nanotubes.

EDS analysis (Figure 3) clearly shows the existence of Ru and the molar ratio of RuO₂ to PEDOT (sulfur on the thiophene group represents the PEDOT) is 0.95:1.

The charge storage mechanism of RuO₂/PEDOT composite nanotubes as the electrode materials for supercapacitors can be illustrated in Scheme 2. Scheme 2 (a) is the overview of the charge/discharge process of composite nanotubes. The electrolyte can easily penetrate into the hollow nanotubular structures and access their internal surface. The electrons that are involved in the redox process are transported by the sputtered platinum on the bottom of the alumina template. Scheme 2 (b) focuses on the detailed charge storage mechanism of RuO₂/PEDOT composite nanotubes. The pseudocapacitance behaviors of these composite nanotubes are originated from the ions diffusions during the simultaneous and parallel redox process of RuO₂ and PEDOT. The thin walls of the nanotubular structures allow the fast ion diffusions owing to their small nanoscaled dimensions. During the charge process, the Ru species expel protons (H⁺) and are oxidized into their higher oxidative forms. At the same time, the neutral PEDOT is also oxidized into its oxidative form and doped with counterions (A⁻, here SO₄²⁻). The discharge process is the reverse step of the charge process, which is the reduction route of PEDOT and Ru species. During these charge/discharge processes, the protons and counterions are simultaneously provided by the protons and sulfate ions from the dissociated sulfuric acid in the water.

The electrochemical properties of RuO₂/PEDOT composite nanotubes were studied using cyclic voltammetry and galvanostatic charge/discharge methods. In order to study the impact of RuO₂ deposition on the electrochemical performances of PEDOT nanotubes, we have compared the CV graphs of the PEDOT nanotubes and RuO₂ loaded PEDOT nanotubes in Figure 4. It is obvious that addition of RuO₂ increase the resulting capacitive current dramatically due to the high specific capacitance of RuO₂. The CV shape of the composite nanotubes resembles the CV shapes from the electrochemical growth of RuO₂ (Figure 1) since the similar redox process is involved in the RuO₂ charge/discharge process as well as in its electrodeposition process. Because the shape of the CV graph is not ideal rectangular shape and the current is not maintained as a stable value, it is difficult to estimate the specific capacitance from the CV graph. Thus the galvanostatic charge/discharge method is also

performed to estimate the specific capacitance and evaluate the power density and energy density.

Figure 5 shows the galvanostatic charge/discharge curve of RuO₂/PEDOT composite nanotubes obtained at the current density of 5 mA/cm² in the standard three electrode system. The high linearity and symmetry of this curve indicate the high charge/discharge efficiency, which is due to the sufficient ion diffusions into/out the thin walls of nanotube during its the charge/discharge process. The specific capacitance can be estimated based on the equation (1), where i is the current used for the galvanostatic charge/discharge experiment, $\Delta V/\Delta t$, potential change rate, can be measured from the reciprocal of the slope on the galvanostatic charge/discharge curve.

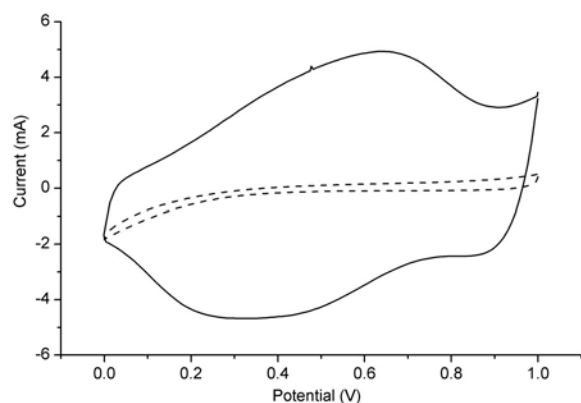


Figure 4. Cyclic voltammograms of PEDOT nanotubes (dotted line) and RuO₂/PEDOT composite nanotubes (solid lines) at the scan rate of 50 mV/s in 1 M sulfuric acid.

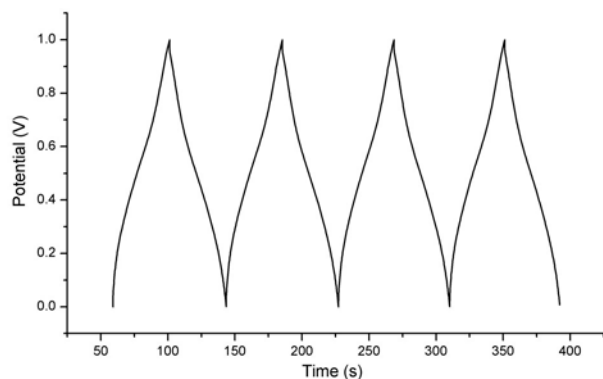


Figure 5. Galvanostatic charge/discharge curve of RuO₂/PEDOT composite nanotubes, at current density of 5 mA/cm² in the electrolyte of 1 M sulfuric acid.

The specific capacitance for the composite nanotube can be directly estimated as 664 F/g based on figure 5. The capacitance of each nanotube can be viewed as the contribution of the capacitance from the PEDOT nanotube and from the RuO₂ which is later

electrodeposited on the PEDOT nanotube since PEDOT and RuO₂ work in a parallel manner.

The specific capacitance of PEDOT nanotube is measured as 150 F/g before the loading of RuO₂ (data not shown), while the specific capacitance of composite nanotube is calculated as 664 F/g as mentioned earlier. The specific capacitance of RuO₂ can thus be derived as 1217 F/g. This specific capacitance value of RuO₂ is much higher than that of the previously reported RuO₂ film, which was also synthesized using similar CV electrodeposition method. The high specific capacitance of RuO₂ is mainly due to its high surface area from the full utilization of RuO₂ with a nanotubular structure. In addition, because the RuO₂ is directly grown on the PEDOT surface, the rough porous PEDOT surface provides additional high surface area to allow the efficient charge/discharge of RuO₂.

CONCLUSION

We have successfully synthesized RuO₂/PEDOT composite nanotubes by a step-wise electrochemical deposition method in an alumina template. The flexible PEDOT and rigid RuO₂ provide mutual mechanical supports to each other. The addition of RuO₂ on the PEDOT nanotubes dramatically enhances the energy density (specific capacitance) of the PEDOT nanotubes. The high surface area from the nanotubular structures allows the better utilization of RuO₂ to realize its high specific capacitance value of 1217 F/g. The thin-walled composite nanotubes provided short diffusion paths and low ionic resistance for the diffusion of counter-ions to make all RuO₂/PEDOT composite materials available during complete charge/discharge even at a fast scan rate.

REFERENCES

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